Chapter One

Introduction and Literature Review

1.1 Introduction:

Photo catalysis can be defined as a change in the rate of chemical reactions or their generation under the action of light in the presence of Substances, called photocatalysts, which absorb light quanta and are involved in the chemical transformations of the reactants. Flash photolysis provides a technique for the study of rapid chemical reactions. It involves the breakup of a molecular species by an intense flash of light (Klingshirn, C. 2007). Then, the absorption lines of the resulting products are monitored to determine the identities and concentrations of the reaction products as a function of the time after the flash. In this way, the course of the chemical reactions may be monitored.

Flash photo catalysis has been used to generate photo chemically, and to study spectroscopically, a wide variety of free radicals and excited molecules (Hoffmann, M. R., & Martin, S.T., & Choi, W., & Bahnemannt D. W. 1995).

Semiconductor photo-catalysis aimed to effectively detoxify noxious organic pollutants. UV light is used to create electron hole pairs in the semiconductor (Gyu-chul Y,Chunrui Wand Won I1P,9 2005 and Thiruvenkatachari R, Vigneswaran S, Moon IS. 2008).

Phenol, the simplest aromatic alcohol, is more acidic than alcohol, due to stabilization of the conjugate base through resonance in the aromatic ring. Since it was first extracted from coal tar in1834, phenol has been widely used in the synthesis of organic chemicals, and has been continuously introduced into the aquatic environment through the effluent from coking plants, petroleum processing plants, chemical plants, pharmaceutical industries, *etc*. Because phenol may be harmful to aquatic ecosystems and present a threat to humans through contamination of drinking water supplies , the removal of phenol has received considerable attention.

Phenol can be removed from effluents by physicochemical methods, such as ozonation , Fenton's reagent , ultraviolet light (UV), by the use of hydrogen peroxide , or by biological methods . In general, biological treatment has advantages over physicochemical methods, as it requires fewer chemical agents and equipment, costs less, and results in less secondary pollution.

1.2 The aim of study:-

To study the effect of ZnO as photo catalysts to reduce some pollutants (phenol- cresol) in drinking water using ultraviolet radiation.

1.3 The problem:-

Phenols are compounds that have one or more hydroxyl groups attached directly to an aromatic ring. Phenol structure is the structure upon which the entire group is based. The aromatic ring in this case is benzene. Phenol is moderately soluble in water- about 8 g of phenol will dissolve in 100 g of water. Phenol is known as human carcinogen and is of considerable health concern, even at low concentration. Phenol can remain in the air, soil, and water for long periods of time if a large amount of it is released at one time, or if it is constantly released to the environment from a source.

1.4 Literature review:

There are many studies are used to treat the concentration of phenol in water such as:

Suja P. Devipriya and Suguna Yesodharan (May 2010) studies Photocatalytic degradation of phenol in water using TiO_2 and ZnO they concluded that:

The results comfirm that the simultaneous presence of catalyst and light is essential for the photodegradation of organics in water. The results reveal that both ZnO and TiO_2 are effective for the removal of phenol from water and the latter is superior in activity. The effect of initial concentration of phenol on the rate of degradation in presence of both ZnO and TiO_2 catalysts was studied, by varying the concentrations over a wide range. The initial rate was calculated from the degradation pattern in the first 30 minutes of irradiation. In the case of both catalysts, the rate increases with increase in initial concentration of the substrate at lower concentration range and the results are consistent with first order kinetics. However at higher concentrations, the increase in rate slows down,

suggesting a reduction in the order of the reaction, as the substrate concentration increases. Interestingly, while the rate of degradation almost levels off in the case of TiO_2, it picks up slowly again in the case of ZnO.

Nafie A. Almuslet and Yasmen H. Zekind (Jan 2013) studies the degradation of Phenol in Water Using Light Induced ZnO Photo catalysis they concluded that:

• Degradation of phenol increases with increasing U.V exposure time.

• The degradation of phenol increases with the increase of the semiconductor Catalyst amount.

Chapter Two
Basic Concepts

2-1 Photo catalysis:

The word "Photo catalysis" is of Greek origin and composes two parts: the" photo" (light) and the word "catalysis "(brake and decompose)

Although there is consensus is scientific community as proper definition of photo catalysis, the term can be generally used describe process in which light is used to activate as substance the" photo catalyst" which modifies the rate of chemical reaction without being involved in it's the chemical transformation. Thus, the main difference between conventional thermal catalyst and photocatlyst is that the former is activated heat whereas is latter activated by photons of appropriate energy.

2-1-1Semiconductors for Photo catalysis:

Many binary compounds are classified as semiconductors, but not all are suitable for photo catalytic applications.

For example, the transition metal dichalcogenides have an attractive structure because the valence band and conduction band are composed of hybridized d-orbital from the metal atoms. Consequently, an electron excitation from the valence band d_{z^2} orbital to the conduction band dxy, $d_{x^2-y^2}$ orbitals does not affect inter atomic bonding and the compounds are generally very resistant to photo corrosion process. This is in contrast to the binary semiconductor compounds, where the valence band character usually is associated with the anion and the conduction band character generally is associated with the cat ion. For these compounds, a band to band transition weakens the inter atomic bond, so photo excitation promotes decomposition and dissolution of the solid when used in solution. For photovoltaic applications, silicon and gallium arsenides have been found to have great practical potential; nevertheless they are not suitable for photo catalytic applications due to lack of chemical stability (Aracely Herna´ndez-Ramı´rez & Iliana Medina-Ramı´rez 2015) .
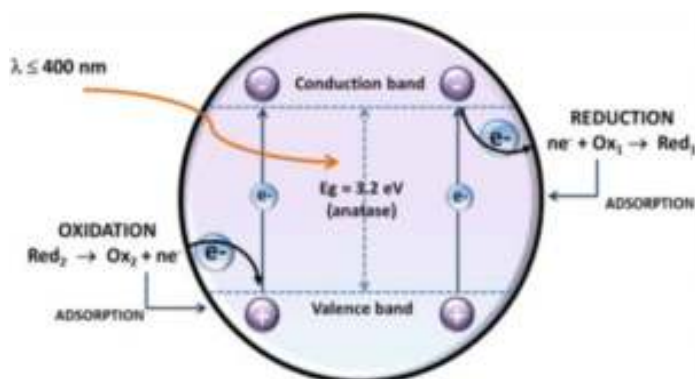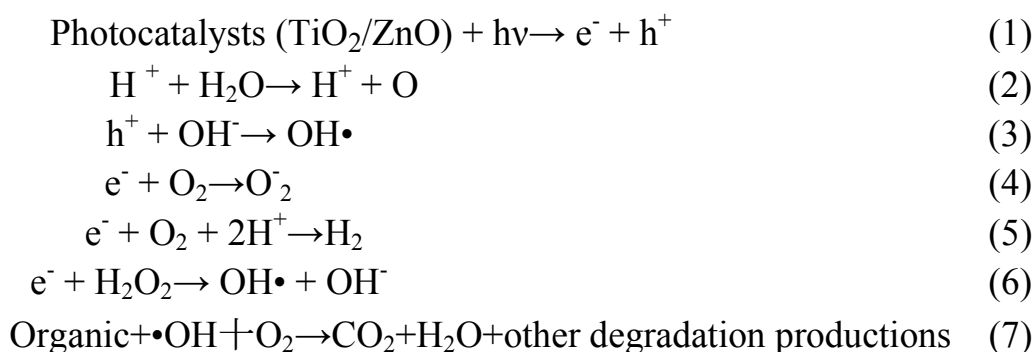
Therefore, an appropriate semiconductor for heterogeneous photo catalysis must fulfill with the following characteristics: appropriate band gap (in the range of 1.7– 3.2 e V), efficient light absorption, high carrier mobility, precise band edge positions that straddle the water red redox

potentials, and nontoxic and chemically stable .Titanium dioxide (TiO_2) in anatase form and zinc oxide (ZnO) in wurtzite phase are the most used metal oxides as photo catalyst due to their electronic band structure and the combination of the properties above mentioned. The band gap (3.2eV) and conduction band edge position of these semiconductors are very similar ($E_{CB} = -0.51V$ at pH 5–7 vs. NHE) are highly efficient Photo catalysts; however, although ZnO is sometimes preferred over TiO₂ for degradation of various organic pollutants due to its high quantum efficiency, it is not stable in acidic aqueous suspensions (Aracely Herna´ndez-Ramı´rez & Iliana Medina-Ramı´rez 2015).

2-1 -2Mechanism of the Photo catalytic Process

The photo catalytic process begins when photons of energy higher or equal to the band gap energy are absorbed by a semiconductor particle and an electron (e^-) from the valence band (VB) is transferred to the conduction band (CB) generating a hole (h^+) in the VB. The absorption of these photons creates within the bulk electron–hole pairs, which dissociate into free photoelectrons in the conduction band and photo holes in the valence band (Aracely Herna´ndez-Ramı´rez & Iliana Medina-Ramı´rez 2015).

The e^- and h^+ can recombine on the surface or in the bulk of the particle releasing the energy as heat or migrate to the surface where they can react with adsorbed molecules on the surface of the particle as illustrated in Fig (1). Frank and Bard first examined the possibilityof using a titanium dioxide-TiO₂ catalyst for the decomposition of cyanide, Ollis and co-workers51 extensively studied the potential application of photocatalysis for organic degradation (Mills A, Davies RH, Worsley D. 1993). Semiconductor photocatalysts generally absorb different colour light depending on their bandgap energy and used as photocatalysts because of their interesting electronic configurations, light absorption ability, charge carrier transport property, and excited-state lifetimes, When a photocatalytic surface is exposed by a radiation of energy equal to or greater than the bandgap energy of the semi-conductor photocatalyst material, it creates a positively charged hole in the valance band and negatively charged electron in the conduction band by exciting the electrons in the valance band to the conduction band (Fan H, Jiang T, Wang L, Wang D, Li H, and Wang P, et al. 2012).

$$\text{Photocatalysts (TiO}_2/\text{ZnO)} + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$H^+ + H_2O \rightarrow H^+ + O \tag{2}$$

$$h^+ + OH^- \rightarrow OH\bullet \tag{3}$$

$$e^- + O_2 \rightarrow O^-_2 \tag{4}$$

$$e^- + O_2 + 2H^+ \rightarrow H_2 \tag{5}$$

$$e^- + H_2O_2 \rightarrow OH\bullet + OH^- \tag{6}$$

$$\text{Organic} + \bullet OH + O_2 \rightarrow CO_2 + H_2O + \text{other degradation productions} \tag{7}$$

Figure (2.1) Schematic of the photocatalytic mechanism for TiO_2 / ZnO photo catalysts.

The conduction band electron reduces oxygen (into O^{2-})adsorbed to photocatalyst surface (TiO$_2$/ZnO) whereas the positively charged hole oxidizes either organic pollutants directlyor indirectly by water to produce hydroxiyl free radicals (HO·).The photocatalytic reaction mechanism shown above (Figure 1) can be described by Eq. (1)-(7) as shown below(Gyu-chul Y,Chunrui Wand Won I1P,92005and Luxon, J. T., & Parker D. E. 1992); In the photocatalysis of the organic pollutants, the oxidation of pollutants and the reduction process of oxygen do not occurs concurrently, there is an accumulation of electrons in the conduction band of thephotocatalyst, thus helping a recombination of negatively charged electron and positive hole. Therefore, efficient utilization of electrons is necessary to encourage photocatalytic oxidation

process. Semiconductors can also be used as photocatalysts forenvironmental remediation. Here, the photon-induced electronholepairs helps in redox reactions at the semiconductors catalyst surface and produces hydroxyl free-radicals (OH•) and superoxide ions (O^{2-}). These generated species act as powerful oxidizer to disintegrate harmful organic pollutants in wastewater and convert them into CO_2 and H_2O. The most significant and fundamental components for a proficient photocatalytic system are the photocatalyst, the light source the reactor configuration (Gyu-chul Y,Chunrui Wand Won I1P,9 2005).

2-1-3Metal Oxides Photo catalytic Semiconductors:

Simple binary oxides with a d-transition metalTiO_2, ZnO, WO_3, and Fe_2O_3have been the most studied metal oxides with photocatalytic purposes, among them, $TiO_2$is the photo catalyst mainly used due to its non toxicity, water insolubility, hydro philicity , low cost, stability, and resistance to photo corrosion.

However, several binary metal oxides have been tested in the photo catalytic degradation of various organic compounds as possible alternatives to TiO_2.

Zinc oxide is an n-type semiconductor whose thermodynamically stable phase is hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron and vice versa. This tetrahedral coordination is typical of Sp3 covalent bonding nature, but this material also has a substantial ionic character that tends to increase the band gap beyond the one expected from the covalent bonding.

Despite this fact, Zn O is the second most employed semiconductor afterTiO_2.Because of its good optoelectronic, catalytic and photochemical properties along with its low cost and nontoxic nature. The band gap value for Zn O semiconductor depends on preparation method because different kind of structural defects can be produced and may alter the electronic structure. Thereby the band gap energy reported for Zn O in various articles varies from 2.8 to 3.37 e V.

The quantum efficiency of Zn O powder is also significantly larger than that of TiO_2 Powder. Higher catalytic efficiencies, in many cases, have been reported for Zn O, but the occurrence of photo corrosion and the susceptibility of Zn O to facile dissolution at acidic pH values have

limited its application in photo catalysis. The photo catalytic advantages offered by Zn O can be exploited by controlling the solution pH at neutral conditions (Aracely Hernaʹndez-Ramıʹrez & Iliana Medina-Ramıʹrez 2015) .

Bandgap energies for anther common semiconductor
Materials at 0 K (Sobczynski A, Dobosz A 2001, Aracely Hernaʹndez-Ramıʹrez & Iliana Medina-Ramıʹrez 2015, Thiruvenkatachari R, Vigneswaran S, Moon IS 2008) .

Table (2-1) Common photocatalytic semiconductors and band gap energy

Semiconductors	Bandgap energy (eV)
Diamond	5.4
Cu_2O	2.172
ZnS	3.60
TiO_2	3.030
SnO_2	3.54
ZnO	3.36
CdSe	1.7
WO_3	2.76
Si	1.170
Fe_2O_3	2.3
PbS	0.286
PbSe	0.165
CdS	2.42

2-2 The electromagnetic spectrum:

Ultraviolet (UV) and visible radiation comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X rays.
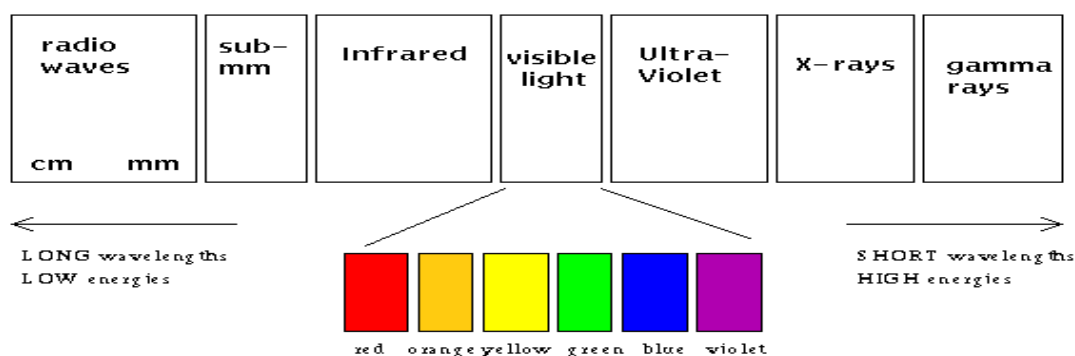
Figure (2.2) Explain the range of electromagnetic radiation

The energy associated with electromagnetic radiation is defined by the following equation:

$$E = hv$$
(1)

Where

E = energy (in joules).

h = Planck's constant (6.62×10^{-34} Js).

v = frequency (in seconds).

2-2-1 Wavelength and frequency:

Electromagnetic radiation can be considered a combination of alternating electric and magnetic fields that travel through space with a wave motion. Because radiation acts as a wave, it can be classified in terms of either wavelength or frequency, which is related by the following equation:

$$v = C/\lambda$$
(2)

Where

v = frequency (in seconds).

c = speed of light ($3 \times 10^8 ms^{-1}$).

λ = Wavelength (in meters).

In UV-visible spectroscopy, wavelength usually is expressed in nanometers ($1nm = 10^{-9}$m).It follows from the above equations that radiation with shorter wavelength has higher energy. Reactions when

measuring sample spectra (remember, it is the UV component of light that causes sunburn).

2-2-3 Origin of UV-visible spectra:

When radiation interacts with matter, a number of processes can occur including, reflection,scattering,absorbance, fluorescence/phosphorescence (absorption and reemission), and photochemical reaction (absorbance and bond breaking). In general, when measuring UV-visible spectra, we want only absorbance to occur.

Because light is a form of energy, absorption of light by matter causes the energy content of the molecules (or atoms) to increase. The total potential energy of a molecule generally is represented as the sum of its electronic, vibrational, and rotational energies:

$$T_{total} = E_{electronic} + E_{vibrational} + E_{rotational} \qquad (3)$$

The amount of energy a molecule possesses in each form is not a continuum but a series of discrete levels or states. The differences in energy among the different states are in the order:

$$E_{electronic} > E_{vibrational} > E_{rotational} \qquad (4)$$

In some molecules and atoms, photons of UV and visible light have enough energy to cause transitions between the different electronic energy levels. The wavelength of light absorbed is that having the energy required to move an electron from a lower energy level to a higher energy level. Formaldehyde and the wavelengths of light that cause them. These transitions should result in very narrow absorbance bands at wavelengths highly characteristic of the difference in energy levels of the absorbing species [19].

2-2-3 Transmittance and absorbance:

When light pass through or is reflected from a sample, the amount of light absorbed is the difference between the incident radiation (I_o) and the transmitted radiation (I). The amount of light absorbed is expressed as either transmittance or absorbance.

Transmittance usually is given in terms of a fraction of 1 or as a percentage and is defined as follows:

$$T = I/I_0 \% \quad \text{or} \quad T = I/I_0 \times 100 \qquad (5)$$

Absorbance is defined as follows:

$$A = - \log T \qquad (6)$$

For most applications, absorbance values are used since the relationship between absorbance and both concentration and path length normally is linear.

2-2-3 Quantitative analysis:

Lambert is credited with the first mathematical formulation of this effect, although it now appears that Bouguer first stated it in 1729[19]. The mathematical expression is:

$$T = I/I_0 = e^{-kb} \tag{7}$$

Where

I_0 = incident intensity.

I = transmitted intensity.

E= the base of natural logarithms, k is a constant, and b is the path Length.

Beer's law is identical to Bouguer's law, except that it is stated in terms of concentration. The amount light absorbed is proportional to the number of absorbing molecules through which the light passes.

Combining the two laws gives the Beer-Bouguer-Lambert law:

$$T = I/I_0 = e^{-kbc} \tag{8}$$

Where

c = the concentration of the absorbing species.

This equation can be transformed into a linear expression by taking the logarithm and is usually expressed in the decadic form:

$$A = -\log T = -\log I/I_o = \log I_o/I = \varepsilon ba \tag{9}$$

Where

ε = the molar absorption or extinction coefficient. This expression is commonly known as Beer's law. The extinction coefficient (ε) is characteristic of a given substance under a precisely defined set of conditions, such as wavelength, solvent, and temperature. In practice, the measured extinction coefficient also depends partially on the characteristics of the instrument used. For these reasons, predetermined values for the extinction coefficient usually are not used for quantitative analysis. Instead, a calibration or working curve for the substance to be

analyzed is constructed using one or more standard solutions with known concentrations of the analyte.

For electronic transitions, the difference in energy between ground and excited states is relatively large. Therefore, at room temperature, it is highly likely that all molecules are in the electronic ground state. Absorption and return to ground state are fast processes, and equilibrium is reached very quickly. Thus absorption of UV-visible light is quantitatively highly accurate.

The simple linear relationship between absorbance and concentration and the relative ease of measurement of UV-visible Concentration light have made UV-visible spectroscopy the basis for thousands of quantitative analytical methods (Tony Owen 1996).

2-2- 3 Instrumental design:

A spectrophotometer is an instrument for measuring the
Transmittance or absorbance of a sample as a function of the wave length of electromagnetic radiation. The key components of a spectrophotometer are:

• a source that generates a broad band of electromagnetic
radiation

• A dispersion device that selects from the broadband radiation
of the source a particular wavelength (or, more correctly, a
waveband)

• A sample area

• One or more detectors to measure the intensity of radiation**.**

Other optical components, such as lenses or mirrors, relay light
through the instrument.

Sources:

The ideal light source would yield a constant intensity over all
wavelengths with low noise and long-term stability.

Unfortunately, however, such a source does not exist. Two
Sources are commonly used in UV-visible spectrophotometers.

The first source, the deuterium arc lamp, yields a good intensity continuum in the UV region and provides useful intensity in the
visible region . Although modern deuterium arc lamps have low noise, noise from the lamp is often the limiting factor in overall instrument noise

performance (the time required for the intensity to fall to half of its initial value) of approximately 1, 000 h.

The second source, the tungsten-halogen lamp, yields good intensity over part of the UV spectrum and over the entire visible range. This type of lamp has very low noise and low drift and typically has a useful life of 10,000 h.
Most spectrophotometers used to measure the UV-visible range
contain both types of lamps.

Detectors: A detector converts a light signal into an electrical signal. Ideally,it should give a linear response over a wide range with low noise and high sensitivity. Spectrophotometers normally contain either
a photomultiplier tube detector or a photodiode detector.
The photomultiplier tube combines signal conversion with several stages of amplification within the body of the tube. The nature of the cathode material determines spectral sensitivity. A single photomultiplier yields good sensitivity over the entire UV-visible range. This type of detector
Yields high sensitivity at low light levels. However, in analytical spectroscopy applications, high sensitivity is associated with low concentrations, which result in low absorbances, which in turn
result in high intensity levels. To detect accurately small differences between blank and sample measurements, the detector must have low noise at high intensity level[19]
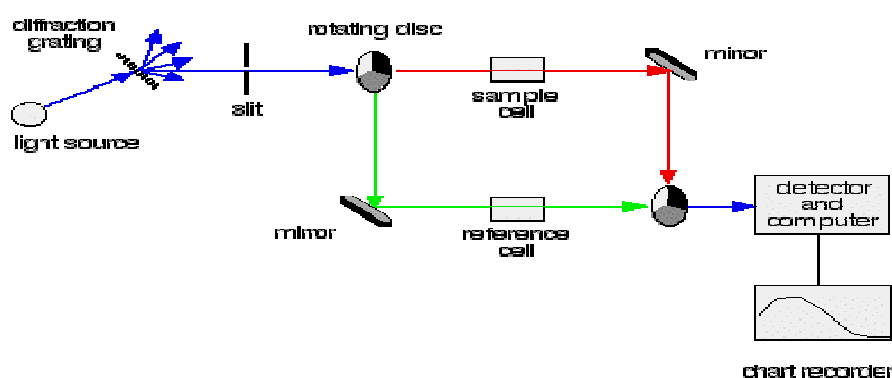

Figure (2.3 w) showing how the ultraviolet/visible spectrometer work

Chapter Three
Experimental work

3-1 Introduction:

This chapter explains the experimental method, material and instrument.

3-2 Materials:

The materials used in this work were:

3-2-1 Ultraviolet\visible spectrometer instrument:

The optical properties of the samples were investigated using UV-VIS spectrometer (U V minimum 1240 SED – SPEC-48) SHIMDZU for the absorbance.
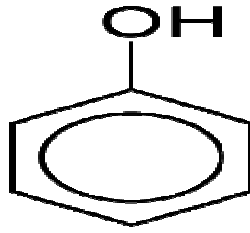

Figure (3.1) shows the instrument was used in this work

3-2-2 Phenol:

Phenols are organic compounds that contain a hydroxyl group (−OH) bound directly to carbon atom in a benzene ring. The structural moiety of phenols in the context of the present chapter is given by structure. Phenol has chemical formula C_6H_6O (Tony Owen 1996).

Figure (3.2) shows the .Structural formula of phenol

Phenol is a colorless-to-white solid when pure, commercial   phenol is a liquid that evaporates more slowly than water and has a distinct odor that is sickeningly sweet, large amounts of phenol are produced in the United. He is used to make plastics, also used as a disinfectant in household cleaning products and in consumer products. Naturally, can be found in air and water after release from the manufacture, use, and disposal of products containing phenol and in soil is likely to move to groundwater.

Figure (3.3) shows the picture of   phenol

Physical   Properties of Phenol:
The table 3.1 shows the physical Properties of Phenol (Health Service Agency for Toxic Substances and Disease Registry, September 2008).

Table 3.1 shows the physical Properties of Phenol [21]

Property	Information
Molecular weight	94.111
Color	Colorless
Physical state	Crystalline solid liquid (w/ 8% H2O)
Boiling point	181.87 °C
Density at 20 °C/4	1.0545 at 45 °C/4
Melting point	40.89 °C
Vapor pressure at 25 °C	0.35 mmHg
Water	7.9 ppm (w/v)
Odor	Distinct aromatic, somewhat sickening, sweet

3-2-4 Zinc oxide:

Zinc Oxide is a unique material with direct band gab (3.37 e V) and large exaction binding energy of $60 m.eV^{-1}$ (Qiuxiang Z, Ke Y, Wei B, Qingyan W, Feng X, Ziqiang Z, Ning D, Yan S,2007, Devipriya, S. P & Yesodharan, S 2010). It has been widely used in near – UV emission, gas sensor and transparent conductor and piezoelectric application. Most of ZnO crystals have been   synthesized   by traditional high temperature solid state method which is energy consuming and difficult to control the particle properties (Hui Z, Deren Y, Xiangyang M, Yujie J, Jin X and Duanlin Q,2004) Li W J, Shi E W, Zheng Y Q and Yin Z W,2001).

3-3 Method:

There are seven samples used in this work were prepared in steps as follow:

-The first sample is distilling water.

-The second sample: is a phenol solution with different concentrations (05 %, 10%, 15%, 20% and 25%).

- The third sample: 5 mg of ZnO was solved into 5 ml of phenol, and then the mixture was filled up to 100 ml by distilling water.

- The fourth sample: 5ml of cresol was added to 5 mg of ZnO and filled up to 100 ml by distilled water.

Lastly was used UV spectrophotometer for recorded spectrum of each simple.

Chapter Four
Result and Discussion

4-1 Introduction:

In this chapter the results of absorption spectrum for different concentration of phenol, absorption spectrum of cresol without photo catalysis and with photo catalysis using UV vis. spectroscopy will be presented and discussed.

4-2 Results and Discussion:

Figure 4.1 below shows the absorption spectra carried out of the distilling water sample as a control, it shows from the figure that the wavelengths greater than 300 nm don't absorbed in contrast of the wavelengths less than 300 nm which is highly absorbed.
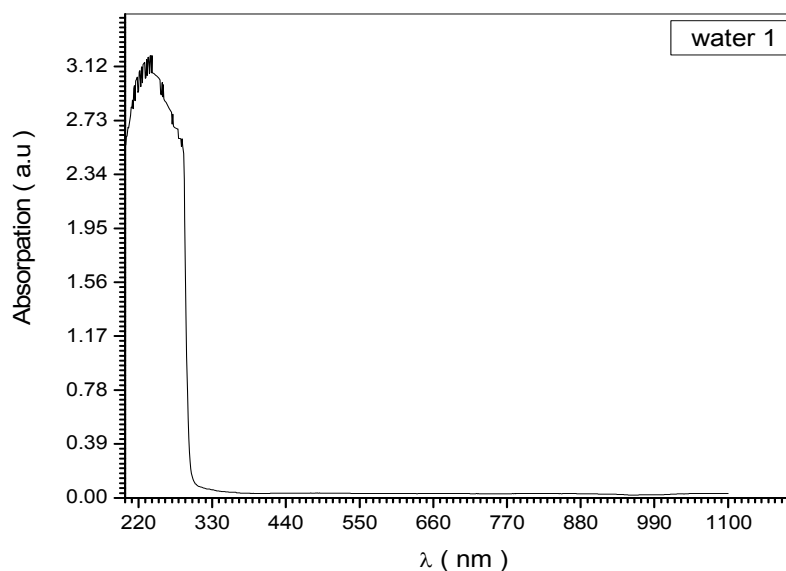

Figure (4.1) Absorption spectrum of 05 % phenol in 100 ml water without photo catalysis, where absorption peak in 240nm

Figure 4.2 below shows the absorption spectra carried out of water and the five samples with different solutions of phenol with concentrations (05 %, 10%, 15%, 20% and 25%). The figure shows that the absorbance is increase with increasing concentration of phenol in water.
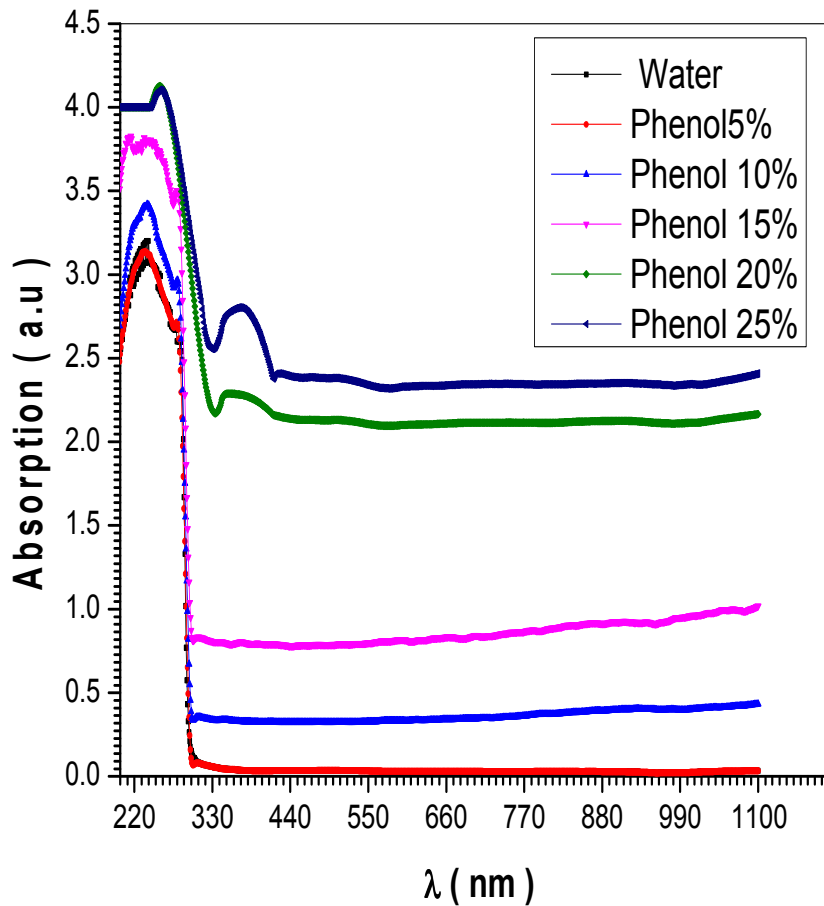
Figure (4.2) Absorption spectra of different concentration   phenol and wavelength

Figure 4.3 below shows the absorption spectrum of phenol solutions with its different concentrations.
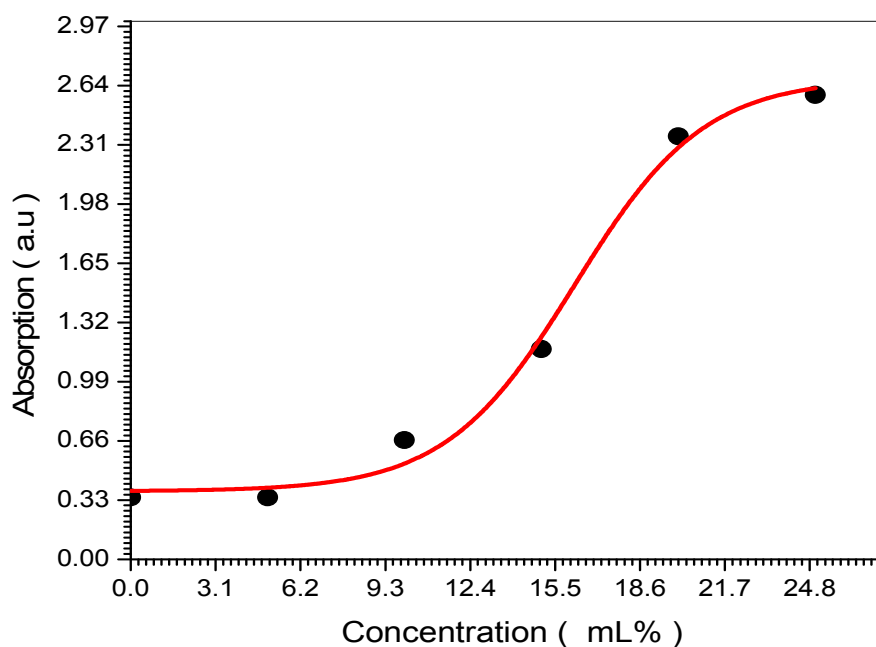
Figure (4.3) shows absorption spectra of phenol and concentration

The figure shows that the absorbance of phenol solutions with its different concentrations is an increase with increasing the concentration of phenol in the water according the Boltzmann equation:

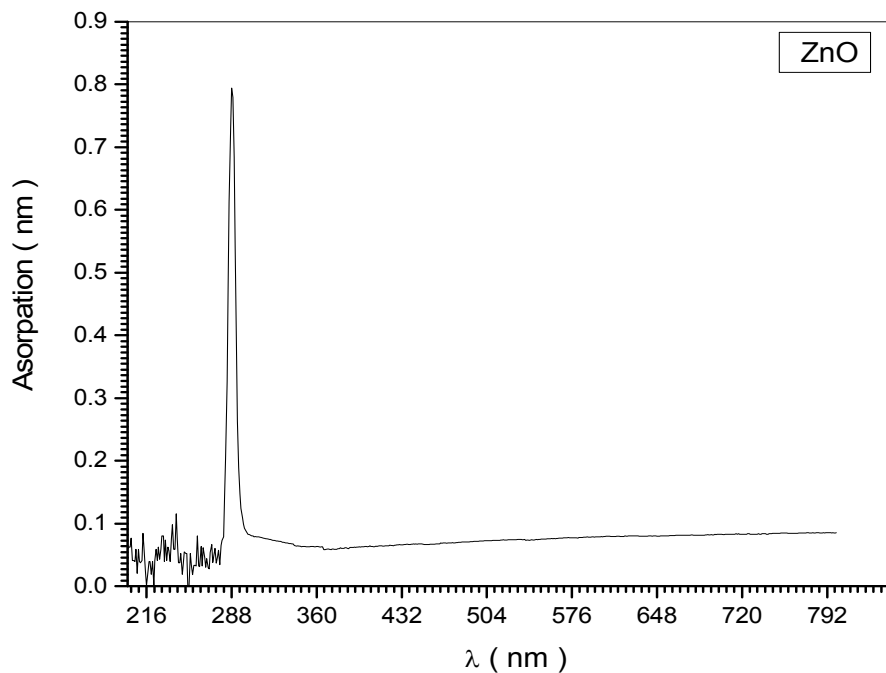$$Absorption = \frac{const}{e^{(c_1 - c_2)/dc}}$$

Where:

Const=5.03

c_1= First concentration

c_2= any concentration in curve

From this equation it is clear that the absorption increase with increasing concentration of phenol which can be calculated in water including the phenol hazardous to humans and animals.

Figure (4.4) Absorption spectrum of 05 % phenol in 100 ml water with ZnO as a photo catalysis, where absorption peak in 288nm

Figure 4.4 shows that the absorption peak of water contaminated with phenol after adding ZnO as a photo catalysis in the range of the UV range, so if it exposure by UV rays the degradation of phenol will increases with the increase of the semi-conductor catalyst amount and increasing UV exposure time as in the previous studies that the concentration of phenol can treated by varies methods such as irradiation of pulled water and suitable catalyst as it was done by Nafie A. Almuslet and Yasmen H. Zekind they found that the degradation of phenol increases with increasing UV exposure time and the degradation of phenol increases with the increase of the semiconductor catalyst amount see the figure (4-5).
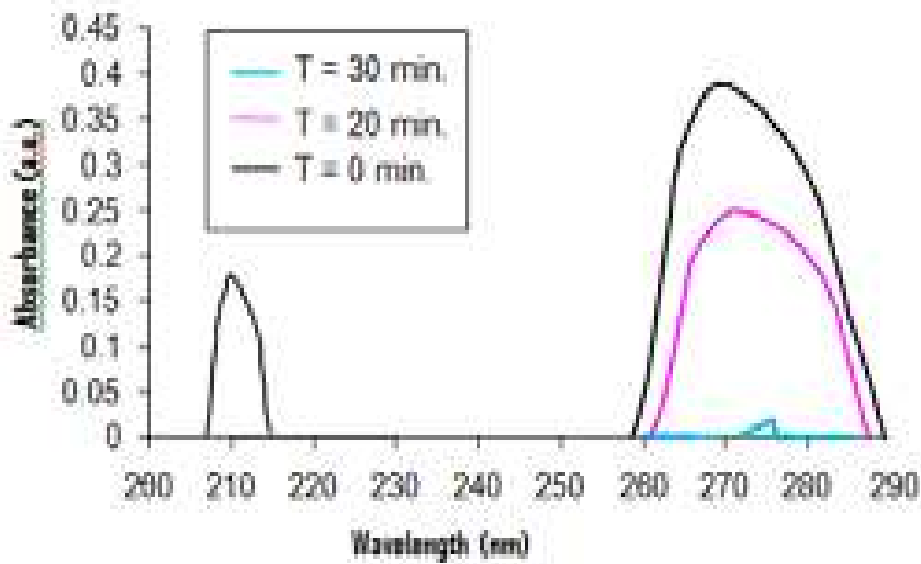
Figure (4.5) The absorption spectra of phenol mixed with 400 mg ZnO irradiated by LED with exposure times of: 0, 20 and 30 minutes. (Nafie *A. Almuslet and Yasmen H. Zekind***)**

4-3 Conclusion:

From the results obtained in this work the followings can be concluded that:

- The UV Vis absorbance of water contaminated with phenol is increase with increasing concentration of phenol in water according to the following Boltzmann equation:

$$Absorption = \frac{const}{e^{(c_1 - c_2)/dc}}$$

- Water contaminated with phenol can be treated using ZnO as a catalysis and UV exposure.

4-4Recommendations:

Future studies could be done by adding for a catalyst working on absorption in the visible range.

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